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Portable Polarographic Reference Electrode. Rolf K. Ladisch and Stanley Knesbach, Quartermaster Pioneering Research Laboratories, Philadelphia, Pa.

THE dropping-electrode process is ordinarily standardized against the potential of a calomel reference electrode within the polarographic circuit. Because calomel half cells with a small mercury surface may develop considerable resistances to the flow of current, owing to concentration polarization or a surface film of mercurous chloride on the mercury (*8*), special electrodes have been recommended, among them the cells of Lingane and Laitinen (*7*), Langer (*5*), and Smith (*12*). Despite the fact that such cells are being widely used in polarography, caution as to their reliability must be exercised, particularly in very precise work such as reported by Meites (*9*). The cells cannot be moved about freely (*1*) and must be kept in an upright position to maintain the original cleanliness of the platinum contact (*2, 3, 6*).

The changes of potential in a number of H-cells arising from the shaking of these cells have been measured in this laboratory. Usually, the measured change in potential traverses a range of not more than 1 mv. within 60 minutes after shaking, but deviations of several millivolts have been observed, especially with cells which had been in use for a number of days. This is in agreement with the findings of Sauer (*11*), who observed inaccuracies of the electrode potential of 1.5 mv. shortly after shaking the contents within the cell, after which the potential acquired the correct value within 5 to 6 hours.

Therefore, it would seem more convenient to use a commercially available rugged reference electrode for pH measurements. However, these cells are intended for systems in which no current is allowed to flow, and because of their small mercury surface they are unreliable at higher current densities in the polarographic circuit. Kolthoff and Lingane object to their use because of their high ohmic resistance (*4*).

A nonpolarizable rugged half cell of low ohmic resistance for polarographic work can be constructed by means of a special but simple arrangement. The basic idea is to confine the mercury in a rigid support such as a glass frit. In choosing a frit of proper size, the area of mercury can be made equal to or even several times that of the conventional mercury pool. Calomel paste is placed in direct contact with the mercury carrying frit. In this manner, the contact between platinum wire and mercury is not disturbed under the conditions of polarographic procedure at any time either mechanically or electrochemically even with frequent handling. Various modifications of this type of cell have been used over a period of 3 months with excellent results.

DESCRIPTION OF CELLS

Various calomel reference electrodes were constructed. Such cells, designated as *A*, *B*, and *C* are reproduced in Figure 1 in cross-sectional views. Corning fritted-glass parts with nominal maximum pore sizes of 40 and 5 microns were used at random. Either a thin platinum wire or an ordinary tungsten-copper lead may be employed to make electrical contact with the mercury. Further details of design are readily recognizable from Figure 1.

To prepare the cells, the part delivered by the glass blower was placed in a desiccator and was evacuated by means of a high vacuum pump for at least 1 hour in each case. Still under vacuum, triple-distilled mercury (Delta Chemical Works) was admitted through a funnel in the lid of the desiccator such that the mercury filled the space around the accessible part of the fritted glass. The mercury penetrated the wall of the coarse frits to occupy the spaces shown in Figure 1 as soon as the vacuum in the desiccator was returned to atmospheric pressure.

With the fine frits of 5-micron pore size, a pressure of 75 pounds per square inch gage from a nitrogen cylinder was applied. This operation was done in a stainless steel bomb, to which the glass part of the cell including the mercury had been transferred from the desiccator. Once the mercury filling was confined in its intended space in the cell, the excess mercury was shaken off.

A paste consisting of mercurous chloride, special for calomel cells (Fisher Scientific Co.) and potassium chloride solution, special for calomel cells (Eimer and Amend) was introduced into cells *A* and *B*, respectively. The preparation of cell *C* was completed by brushing the mercurous chloride–potassium chloride paste onto the surface of the frit. In this case, 0.35% by weight of agar had been included in the potassium chloride solution before making up the paste.

Cell *C* was also constructed in a modified form (not pictured). In this case, the wire contact was omitted and the glass part was left open at this place. Calomel–potassium chloride paste was deposited within the wall of the fritted glass by suction with a water injection pump in a manner similar to ordinary filtration practice. Thereafter, the cell was cleaned internally several times with distilled water. Air was sucked through the fritted glass until it was dry. The free space in the cell was filled with mercury to a height comparable with the one shown in Figure 1, cell *C*. The contact wire was inserted, and the cell was sealed off by electrical insulating cement.

EXPERIMENTAL

The potential of the new cells were checked in saturated potassium chloride solution against a previously standardized Beckman calomel electrode, Type 1170, in combination with a Rubicon potentiometer No. 2780 and a Rubicon galvanometer No. 3405 HH. Deviations from 0.08 to 0.60 mv. were observed with the freshly made reference electrodes, the average value for all the cells being 0.3 mv. The electrodes came to equilibrium overnight and then showed even more accurate potentials well within 0.3 mv. of the theoretical value.

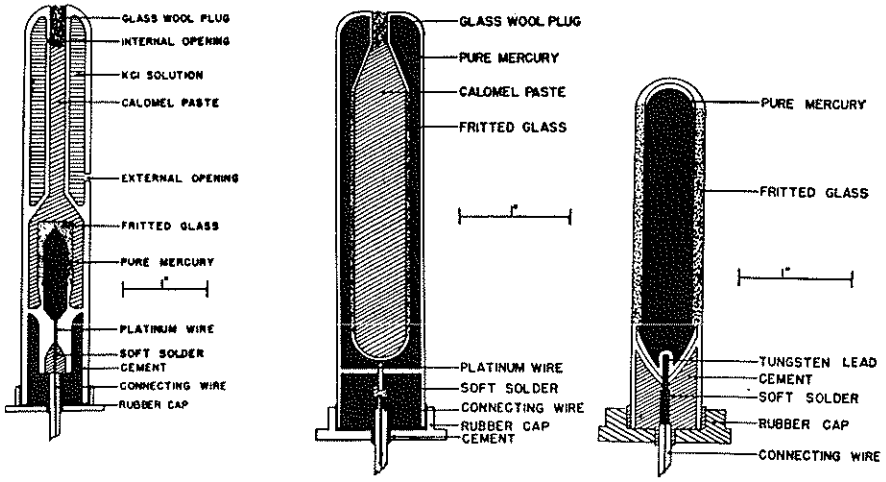

Figure 1. Cross-Sectional Views of Cells

In the course of several weeks, a great number of analyses of 1.00 and 2.00*mM* cadmium sulfate in 0.1*N* potassium chloride solution were performed. The reference electrodes were immersed into saturated potassium chloride solution in one arm of an H-type polarographic cell, while the other compartment of the H-cell contained the test solution separated by an agar plug

as usual. The resistances in ohms (*10*) across the polarographic circuit were as follows:

	Cell			
Test solution	*A*	*B*	*C*	*D*
1*mM*	1560	1230	...	...
2*mM*	1480	1170	1140	1120

In comparison, a conventional mercury pool electrode in the otherwise identical system gave resistances of 1310 and 1160 ohms for the 1.00 and 2.00*mM* test solutions, respectively.

The new reference electrodes were handled frequently during the course of these investigations. Because of this and their excellent stability, they should be particularly suited for routine polarographic analysis.

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